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6. AUTHOR(S) Kenneth A. Mauritz and Robson F. Storey	

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of So. MS Dept. Of Polymer Science Box 10076 Hattiesburg, MS 39406-0076	8. PERFORMING ORGANIZATION REPORT NUMBER

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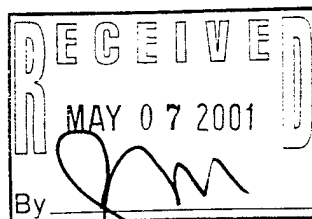
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I. GENERAL INTRODUCTION

The mission of this research is to create lightweight elastomers that ultimately can be used in clothing that protects soldiers from chemical warfare agents (CWAs). Outward transport of water from perspiration is another important requirement. Our hypothesis is that the simultaneous fulfillment of these requirements is possible through the manipulation of the heterogeneous architecture followed by the inorganic modification of hard/soft block copolymer (BCP) elastomers. Our approach consists of selectively inserting a hydrophilic silicate component within sulfonated hard block domains in block copolymer ionomers (BCPIs) via·[2] ·· ᴈ sol-gel reactions for hydrolyzed silicon alkoxides.

The BCPs of primary interest are based on polyisobutylene (PIB) elastomeric center blocks and glassy polystyrene (PS) outer blocks. These materials are suited for this application due to the excellent barrier properties of PIB and the fact that current CWA protective clothing is fabricated from butyl rubber, which is predominantly PIB with a small fraction of functional monomers for crosslinking. The fully saturated hydrocarbon nature of PIB makes it inert toward sulfonation and sol-gel reactions that are later carried out within and around the hard domains. The precursor poly(styrene-¾isobutylene-¾styrene) (PS-PIB-PS) block copolymer elastomers, and sulfonated ionomers derived therefrom, are prepared using controlled/living carbocationic polymerization. Figure I-1 shows various architectures currently being explored including linear triblock copolymers (**L-1**), multi-arm star-block copolymers (**T-1** and **S-1**), and triblock copolymers with tapered copolymer outer blocks (**L-4**). Unique telechelic polyisobutylenes possessing silicon alkoxide functional groups at chain termini (**L-2**) and BCPs possessing such groups at the block junctions (**L-3**) are also targeted. The latter will promote the formation of covalent linkages between organic and inorganic phases.
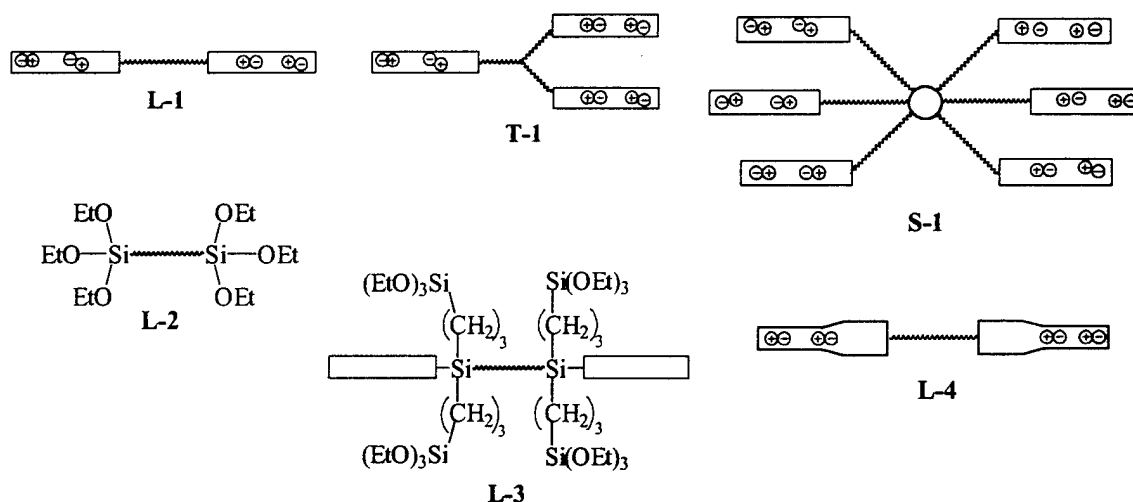

Figure I-1. Various PIB-based elastomeric matrix polymers.

Sulfonated BCPIs serve the role of [3] ꝓ° ᵾꝓ· ½ ´ ᴈ³ ° ¿ ᴈ- that direct · [2] ·· ᴈ sol-gel reactions for silicon alkoxides with the goal of creating elastomeric organic-inorganic hybrid materials with specific diffusion properties. BCPI swelling agents that facilitate selective

migration of hydrolyzed $Si(OR)_4$ monomers to ionic domains are critical. Hydrolyzed tetraethylorthosilicate (TEOS) molecules undergo reactions, $Si(OH)_4 + Si(OH)_4 \rightarrow (HO)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O$, etc., so that silicate nanoparticles incorporate about ionic domains, as depicted in Figure I-2.
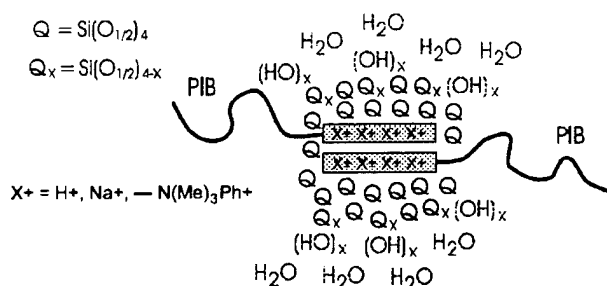

Figure I-2. Sol-gel-derived silicate nanostructure incorporated around an ionic hard block domain.

As seen in our earlier efforts to create [organic polymer]/silicate hybrid materials, a large population of SiOH groups can be made to reside at the "surfaces" of these nanoparticles.[1,2,3,4] SiOH groups impart the following three important functions:

(1) SiOH groups are hydration sites that will facilitate water transport, given long range structuring of water by extended silicate nanostructures that conform to the hard domains in the BCPI phase separated morphology.

(2) Sarin, Tabun, Soman and VX CWAs have strong proton acceptor groups, · ò., P=O, that can bind to SiOH moeities on silicate nanostructures. This complexation might block CWAs from traversing barrier materials. Sulfur mustard (SM), $Cl(CH_2)_2S(CH_2)_2Cl$, is barely soluble in water and the solubilized fraction hydrolyzes after formation of an intermediate sulfonium ion. Natural avoidance of the hydrated domains in Figure I-2 will cause diffusive pathways of SM to be tortuous and pores in the silicate nanoparticles may trap these molecules in a fashion similar to the action of microporous activated carbon fillers in current CWA clothing fabrics.

(3) Resistance to degradation by exposure to petroleum products will result from unfavorable interactions between hydrocarbon molecules and polar SiOH groups. This concept is reinforced by our demonstration that poly(ethylene-½-methacrylic acid) films can be made more resistant to hydrocarbon solvents by the incorporation of a silicate phase via an · 2 -· ·ə sol-gel process.[5]

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II. ORGANIC SYNTHESIS COMPONENT

A. INTRODUCTION AND RATIONALE OF SYNTHETIC STRATEGY

The primary goal of the synthetic effort was and continues to be the creation of BCPs with potential for dramatically increased hydration degrees after inorganic modification. Our approach has been to increase the relative PS volume such that it falls within the range of lamellar morphologies after sulfonation. Since renewal of the project, more specific attention has been paid to the elimination of chain coupling via electrophilic aromatic substitution (EAS) at the 4-position of the styrene rings (as described in the report for 1998 and 1999 activities). The occurrence of such coupling prevents the formation of uniform triblock copolymers due to a broad size distribution of the PS hard segments as well as the presence of pentablock copolymers in the final product. In order to minimize this side reaction, we have worked to develop BCPs with copolymer hard segments containing °ómethylstyrene (°MSt), which is impervious to EAS and sulfonation, copolymerized with either styrene or α-methyl styrene (αMSt). Introduction of a third monomer also raises the possibility for a third morphological phase. The hard segment of the BCP serves two functions: it aggregates into domains that constitute physical crosslinks, thus providing mechanical integrity, and it incorporates hydrophilic sites (after modification), thus providing a pathway for water transmission. If modification of the hard segment is such that it becomes overly hydrophilic, it might imbibe sufficient water to severely compromise mechanical properties. Creating a tapered hard segment, i.e., one in which the °-blocked monomer units are more concentrated within the inner region nearer to the PIB rubbery block, may enable the hard segment to perform its two essential functions more effectively. Such tapering may naturally occur during living copolymerization, since the earlier formed section of the styrenic block will be disproportionately enriched with the more reactive monomer.

A second issue addressed during this reporting period is the occurrence of inefficient crossover from the rubbery PIB centerblock to the PS endblocks. Initiation of styrene by the PIB chain ends is slow in the traditional sense that a substantial fraction of the styrene charge is consumed before all PIB ᵗᵉᵗᵗ-chloride sites have initiated. This effect is particularly strong due to a high run number for each ionization event (a large number of monomer units added prior to ion-pair collapse). Sluggish crossover allows some end blocks to increase in molecular weight rapidly while others have yet to add a first styrene monomer unit, resulting in a high molecular weight distribution of the final product. To remedy this problem, we have employed the method of Faust,[6] whereby diphenylethylene (DPE), a non-homopolymerizable, but highly reactive olefin (see Figure II-1), is used to cap the living PIB chains prior to addition of the styrenic monomer(s). Addition of one DPE unit to each end of the difunctional PIB chain ensures 100% ionization of the living chains and results in immediate crossover upon the addition of the styrenic monomer charge.[6]
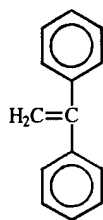

Figure II-1. Chemical structure of DPE

Synthetic efforts toward the polymerization of isobutylene and the various styrenic monomers have been greatly facilitated by our ReactIR™ 1000 reaction analysis system (real-time, remote, light conduit type ATR-FTIR spectrometer, ASI Applied Systems).[7] This instrument was acquired through the DOD DURIP program and is equipped with a DiComp™ (diamond-composite) ATR (attenuated total reflectance) insertion probe, a general purpose PR-11 platinum resistance thermometer (RTD) and CN76000 series temperature controller (Omega Engineering). It is ideally suited for polymerization kinetics measurements by providing continuous monitoring of monomer concentration through collection of IR spectra of the polymerization components, and reactor temperature, in real time.[8,9] With these capabilities, information concerning the extent of reaction and the reaction rates of the various styrenic monomers can be acquired with relative ease.

B. EXPERIMENTAL

1. Materials

5-*t*-Butyl-1,3-di(2-chloro-2-propyl)benzene (bDCC) was prepared from 5-*t*-butyl-isophthalic acid (Amoco Chemical Co.) through esterification with methanol followed by a Grignard reaction to form the *t*-alcohol.[10] The latter was converted to the *t*-chloride by reaction with dry HCl in methylene chloride.[11] Reaction progress was monitored by ^{1}H NMR and the resulting bDCC was twice recrystallized from hexane at 7°C. Synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl) has been described.[12] Styrene, °-methylstyrene (°MSt), α-methylstyrene (αMSt) and diphenylethylene (DPE) (Aldrich Chemical Co.) were freshly distilled from calcium hydride prior to use. Isobutylene (IB) and methyl chloride (MeCl) (BOC Gases) were dried by passing the gaseous material through a column packed with $CaSO_4$ and molecular sieves. Methylcyclohexane (MCHex) (99+% anhydrous, packaged under nitrogen in SureSeal® bottles), TiCl₄ (99.9%, packaged under nitrogen in SureSeal® bottles), 2,4-lutidine (99%, 2,4-dimethylpyridine, DMP), and anhydrous methanol (MeOH) were used as received from Aldrich Chemical Co.

2. Synthesis of Block Copolymers by Sequential Monomer Addition

The following is a representative polymerization procedure for P°MSt-PIB-P°MSt: the DiComp probe was fitted into a stainless steel scabbard, and this assembly was allowed to equilibrate in the –70°C heptane bath. The probe remained stationary from this point forward. After acquisition of a background spectrum, the bath was partially drained, the scabbard was removed, and a 250 mL, four-necked round-bottomed flask, equipped with a mechanical stirrer, was fitted around the probe. The bath was then raised to an appropriate level around the flask and maintained at -70 °C. Into the flask was charged 96 mL MCHex, 64 mL MeCl (MCHex/MeCl, 60/40 v/v), 0.056 g (2.0×10^{-4} mol) *t*-Bu-*t*-DCC, 0.05 mL (4.4×10^{-4} mol) 2,4-DMP, and 13.83 mL (1.8×10^{-1} mol) IB. The solution was stirred for about 15 min before commencing polymerization by rapid injection of 0.65 mL (5.9×10^{-3} mol) TiCl₄ (neat and at room temperature). After approximately 5 h (IB conversion > 99% as determined by ReactIR analysis), a 5 mL aliquot was removed from the reaction vessel and added to 10 mL anhydrous MeOH (-70 °C). Next, 0.12 mL DPE (6.9×10^{-4} mol) was charged to the flask and allowed to stir for approximately 20 min. At this point, 4.4 mL (0.032 mol) °-methylstyrene diluted with 20.7 mL of 60/40 (v/v) MCHex/MeCl cosolvents was added to the active polymerization medium to begin P°MSt block formation. Aliquots were removed from the reactor at various

times and precipitated into separate 10 mL portions of anhydrous MeOH (-70 °C), and the remainder of the reactor contents was quenched at 98% monomer conversion with 20mL anhydrous MeOH (-70°C). After quenching, the polymer solution was transferred to a 500 mL beaker, and the solvents were allowed to evaporate overnight. The BCP was dissolved in the appropriate mixture of hexane and methylene chloride and precipitated into ethanol. The final polymer product was collected by vacuum filtration and dried at room temperature in a vacuum oven for 48 h.

All block copolymerizations were conducted in the same manner with the following exceptions: block copolymers were synthesized containing end blocks of PS, P°MSt, PαMSt, P(styrene-co-°MSt) and P(αMSt-co-°MSt) by maintaining the same total styrenic monomer concentration, but varying the monomer feed ratio. Also, due to slow reaction rates at high conversion in the synthesis of homopolystyrene end blocks, the monomer concentration for the desired molecular weight was doubled and the polymerization was quenched at 50% monomer conversion. Finally, BCPs with end blocks containing αMSt were dissolved in toluene before precipitating into ethanol.

3. Real-time ATR-FTIR Monitoring of Block Copolymerization

Block copolymer formation was monitored using the ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond-composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT). This instrument enabled the collection of infrared spectra of the polymerization components and monitoring of reaction temperature in real time. First, the polymerization of IB was monitored by following the diminution and eventual disappearance of the absorption at 887 cm^{-1} associated with the $=CH_2$ wag. By plotting peak height of the absorbance vs time, a monomer decay profile for isobutylene was generated, an example of which is shown in Figure II-2. This particular profile indicates that complete IB consumption occurred at a reaction time of approximately 18,000 s (5 h). The peak height at 887 cm^{-1} at any time, $\varnothing_T$, less the reference peak height, $\varnothing_\alpha$, measured prior to addition of monomer to the reactor, was assumed to be directly proportional to isobutylene monomer concentration. First-order plots were constructed by plotting $\ln\{[M]_o/[M]\}$ vs. reaction time, where $[M]_o/[M] = (\varnothing_\pm - \varnothing_\alpha)/(\varnothing_T - \varnothing_\alpha)$ and $\varnothing_\pm$ is the height of the monomer peak prior to addition of $TiCl_4$. Next the PIB chain ends were capped with DPE. Quantitative monitoring of DPE depletion could not be performed due to insufficient concentration. However, the peak at 912cm^{-1} associated with the $=CH_2$ wag of DPE was monitored qualitatively, and upon its disappearance a charge of styrenic monomer was added to affect blocking. Analysis of styrene depletion was conducted similarly to that of isobutylene, using the peak at 910cm^{-1} associated with the $=CH_2$ wag. However, the polymer chains were already living at the time the styrene monomer was introduced; therefore, $\varnothing_\pm$ could not be directly measured and instead was set equal to the first-measured height of the 910 cm^{-1} peak immediately after addition of the styrene monomer charge.
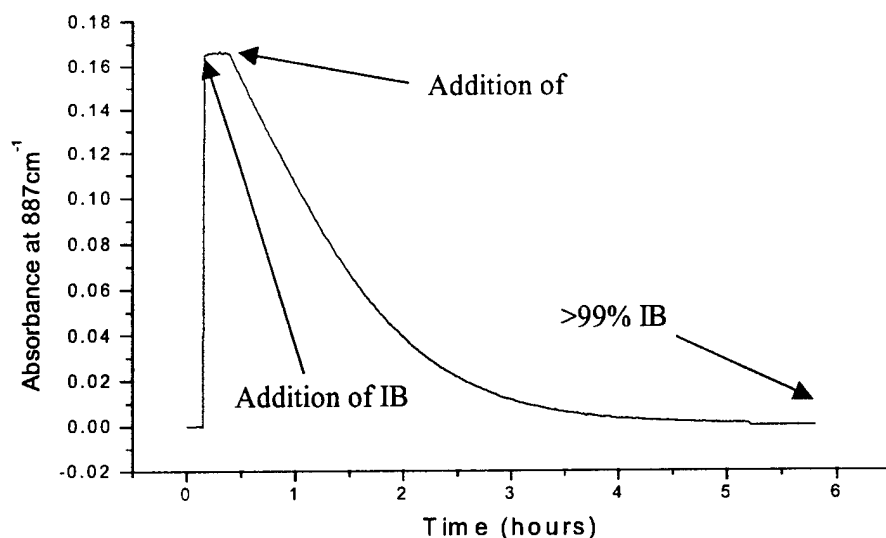
Figure II-2. Monomer decay profile of isobutylene consumption.

4. Determination of Crossover Efficiency by Model End Block Polymerizations

The Dicomp probe was fitted into a stainless steel sleeve, and this assembly was allowed to equilibrate in a heptane bath at $-70°C$. The probe remained stationary from this point forward. After acquisition of a background spectrum, the bath was partially drained, the scabbard was removed, and a 250 mL, four-necked round-bottomed flask, equipped with a mechanical stirrer, was fitted around the probe. Into this reaction vessel was charged a solvent system consisting of 105 mL of MCHex and 70 mL of MeCl, 66 μL of TMP-Cl initiator (3.9×10^{-4} mol), and 51 μL of DMP (4.4×10^{-4} mol). The cold bath was then raised and the contents of the flask were allowed to stir for 15 min, thus establishing thermal equilibrium as indicated by the RTD. In order to mimic a block copolymerization by sequential monomer addition, 0.65 mL TiCl$_4$ (5.9×10^{-3} mol) was added next, thereby activating the TMP-Cl (establishing the ionization equilibrium). DPE, 138 μL (7.8×10^{-4} mol), was then charged to the flask and allowed to stir for approximately 20 min to ensure complete reaction with TMP-Cl. At this point, the TMP-DPE species closely resembles a DPE-capped PIB chain end in terms of both structure and behavior. °MSt, 4.35 mL (3.32×10^{-2} mol), was then charged to the flask, and aliquots were collected at various reaction times and quenched immediately in MeOH. The reaction was allowed to proceed for 75 s and then quenched using methanol. The resulting polymer was rinsed several times with methanol, dried under vacuum for 24 h, and analyzed for composition and molecular weight by ^{1}H NMR and GPC, respectively.

Reaction conversion during the °MSt polymerization was determined using the ReactIR 1000 by monitoring and integrating the area of the peak centered at 909 cm^{-1}. In some cases, the styrenic monomer charge consisted of a 1:1 ratio of styrene/°MSt or α-MSt/°MSt, in which case the combined =CH$_2$ wag of both styrenic monomers at 909 cm^{-1} was monitored. Data were collected at a rate of 2.6 transients per second, and every 4 transients were compiled into a

8

spectrum. As before, $\emptyset_+$ was set equal to the first-measured height of the 910 cm^{-1} peak immediately after addition of the styrene monomer charge.

To determine the effectiveness of DPE capping, the same reaction was conducted without the use of DPE, such that polymerization of °MSt was initiated directly by TMP-Cl cations.

5. End Block Copolymerizations for the Determination of Percent Composition

The percent composition of copolymers containing PIB inner blocks and styrene/°MSt copolymer outer blocks was determined by ^{1}H NMR spectroscopic analysis. However, it was not possible to collect similar data from copolymers consisting of α-MSt/°MSt outer blocks due to peak overlap between the styrenic repeat units and the PIB chain. Therefore, model end block copolymerizations were conducted from a TMP-Cl initiator capped with DPE. These polymerizations were conducted in the same manner as those described above, except that the styrenic monomer charge consisted of a 1:1 ratio of α-MSt : °MSt. The analysis by ^{1}H NMR remained unchanged.

6. Gel Permeation Chromatography (GPC)

Molecular weights and polydispersities (PDI) of the polymeric materials were determined using a size exclusion chromatography (SEC) system equipped with a Waters Alliance 2690 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector (MiniDAWN ^{TM}, Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP ^{TM}, Wyatt Technology Inc.), and two sets of PLgel ^{TM} (Polymer Laboratories Inc.) SEC columns. One set of columns was designed for samples with molecular weights under 30,000 g/mol and the other for molecular weights between 30,000 and 50,000 g/mol. Tetrahydrofuran (THF), freshly distilled from CaH$_2$, was employed as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 7 mg/mL with an injection loop volume of 100μL.

The detector signals were simultaneously recorded using ASTRA ^{TM} software (Wyatt Technology Inc.) for the calculation of absolute molecular weight determined by MALLS and the dn/dc value by the signal response from the Optilab DSP and assuming 100% mass recovery from the columns.

Samples of PαMSt analyzed for crossover efficiency displayed RI responses that exceeded the capacity of the detector in the THF system. In those cases, molecular weights were determined using a different SEC system equipped with a Waters 515 HPLC pump, an Alcott 728 Autosampler (Alcott Inc.), a 2410 Refractive Index Detector (Waters Corp.), and one of two sets of PLgel ^{TM} (Polymer Laboratories Inc.) SEC columns identical to those described above. Freshly distilled CHCl$_3$ served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were ca. 5-10 mg/mL in freshly distilled CHCl$_3$, and the injection volume was 100 μL. The SEC columns were calibrated using a series of narrow polystyrene standards with molecular weights ranging from 580 g/mol – 377,000 g/mol (flow marker = toluene). PL Caliber® GPC software (Polymer Laboratories Inc.) calculated molecular weights and polydispersities by converting the refractive index detector response of the sample into a molecular weight distribution based on the log M vs. elution time calibration curve.

7. Proton Magnetic Resonance Spectroscopy (^{1}H NMR)

^{1}H NMR was used to determine block copolymer composition. Spectra were obtained on either a 200 (AC-200) or 300 MHz Bruker spectrometer using 5mm o.d. tubes. Sample

concentrations were 5-10% (w/v) in chloroform-d containing 0.03% (v/v) TMS as an internal reference (0 ppm). Each spectrum was the Fourier transformation of 32 transients.

C. CAPPING WITH DPE TO IMPROVE CROSSOVER EFFICIENCY IN DMST-PIB-DMST SYNTHESIS

In the report for activities in 1999, it was stated that the crossover from the PIB centerblock to the PS end block is sluggish in the sense that a substantial fraction of the styrene charge is consumed before all PIB $\pi^{\oplus}$-chloride sites have initiated. This phenomenon can be understood in terms of the Winstein spectrum, shown in Figure II-3. Under the quasiliving carbocationic polymerization conditions used herein, the growing chain ends exist either as a covalent tert-chloride species or as a contact ion pair. These two types of chain ends are in rapid equilibrium with each other. In the case of IB polymerizations, the equilibrium constant is quite low (the equilibrium lies far to the left in the Winstein Spectrum) such that only a small fraction of PIB chains can initiate a styrene monomer unit at any given time. In addition, once the first styrene unit has added, the resulting polystyryl cation has a sufficiently high run number (the number of monomer units added prior to ion-pair collapse), that those end blocks which have already initiated can consume a significant fraction of the monomer before other chains have a chance to add the first styrene monomer unit. Such behavior results in a final polymer product containing a broad distribution of end block lengths, and therefore high polydispersity, and in extreme cases a substantial fraction of chains that do not cross over at all (poor crossover efficiency).
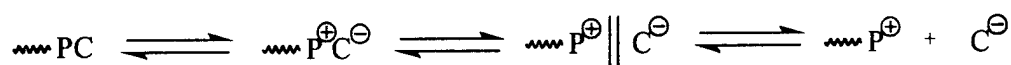

Figure II-3. Representation of the Winstein Spectrum where P is the polymer chain end and C is the counter ion.

In an effort to improve the efficiency of crossover, block copolymerizations were conducted in which the PIB chains were capped on each end with one molecule of DPE. The two phenyl rings conjugated with the DPE cation supply a high level of resonance stabilization. For this reason, the DPE chain ends are considered to be fully ionized and capable of complete initiation of the end blocks immediately upon addition of the styrene monomer charge (See Figure II-4). Once one DPE unit has been added to the PIB chain end, it is unlikely that another will add due to steric hindrance provided by the phenyl rings. Therefore, it's possible to obtain a fully ionized chain end without significantly changing the composition of the polymer.[6]
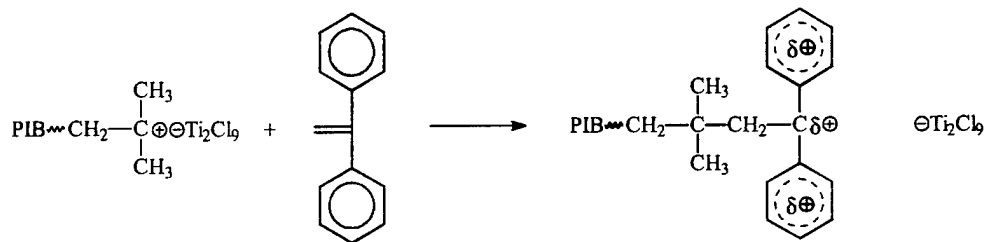

Figure II-4. Addition of DPE to PIB cation allows full ionization of the chain end.

To test the necessity and effectiveness of DPE capping, block copolymerizations were conducted with and without its use. °MSt typically exhibits crossover efficiencies that are lower than those of styrene. For this reason, °MSt was used as the end block monomer in order to produce a more drastic contrast between block copolymerizations conducted with and without the use of DPE. GPC was used to determine molecular weights and molecular weight distributions of aliquots taken at various times throughout the reaction, and conversions at these reaction times were determined using ReactIR analysis. This information along with Equation II-1 was used to calculate the crossover efficiency of each system,

$$\acute{Y}_{,\infty}(\%) = \frac{°[\acute{O}]_{\pm}}{\grave{E}_{,}[\gamma]_{\pm}}100\%$$

Eq. II-1

where ° is conversion, $[M]_o$ is the initial monomer concentration, X_n is the degree of polymerization, and $[I]_o$ is the initial initiator concentration.

The information in Table II-1 shows that the polymerization conducted without the use of DPE suffers from inefficient crossover, as evidenced by the presence of molecular weights higher than targeted early in the reaction.

Table II-1. Crossover Efficiency from Quasiliving PIB to _p_MSt, at Various pMSt Conversions, With and Without DPE Endcapping of the PIB Chains

No DPE			DPE		
Reaction Time (sec)	Conversion[a] (%)	C_{eff}[b] (%)	Reaction Time (sec)	Conversion (%)	C_{eff} (%)
10	49	18	15	61	97
18	59	29	32	88	80
61	99	43	53	99	109

[a]ReactIR data.
[b]GPC data.

D. ELIMINATION OF CHAIN COUPLING THROUGH USE OF ÐMST

Previous reports have shown evidence of chain coupling occurring via electrophilic aromatic substitution (EAS) at the °¿®¿-position of the phenyl rings on the PS end blocks of these copolymers. The occurrence of this side reaction prevents the formation of uniform triblock copolymers due to a broad size distribution of the PS hard segments as well as the presence of pentablock copolymers in the final product (See Figure II-5).
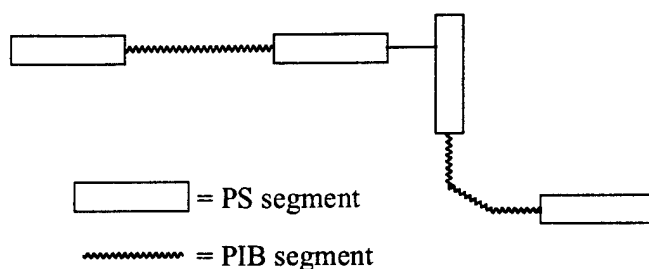
= PS segment

= PIB segment

Figure II-5. Typical product from intermolecular chain coupling reactions during styrene polymerization.

Studies conducted during this reporting period have concentrated on the development of PIB-based BCPs with copolymer outer blocks consisting of poly(styrene-½±°MSt). Such BCPs should be less susceptible to EAS coupling since a certain fraction of the monomer units within the end blocks would be blocked at the °-position, which is the most likely position for attack. Of course, these repeat units would also be unavailable for sulfonation, so it is important that an appropriate fraction of unblocked styrene units also be present. Also of significance is the manner in which the comonomers are incorported. °MSt is suspected to have a significantly faster rate of polymerization than styrene, which may result in an end block microstructure that contains a higher percentage of °MSt at the inner region nearer to the PIB rubbery block.

To investigate the manner of incorporation of °MSt, block copolymerizations were conducted using either pure styrene, pure °MSt, or a 1:1 molar ratio of styrene:°MSt as the outer-block-forming monomer. The reaction involved a target degree of polymerization, X_n, of approximately 91 (M_n = 10,000 g/mole) for the end blocks. The reaction was terminated at 12,000 s reaction time and 87% conversion.

The major infrared absorbances associated with the vinyl group of styrene and °MSt are nearly identical in terms of frequency and intensity. Therefore, it was possible using infrared monitoring to follow the combined consumption of both monomers. The 910 cm^{-1} band proved to be the best of the three major bands, since it is by far the most intense and is relatively free of competing absorptions due to polymer or Lewis acid. First, end block homopolymerizations of each monomer were monitored, and the data were arranged into the first-order plot shown in Figure II-6. It is clear from the plot that °MSt polymerizes significantly faster than styrene, supporting the possibility of a tapered end block copolymer.
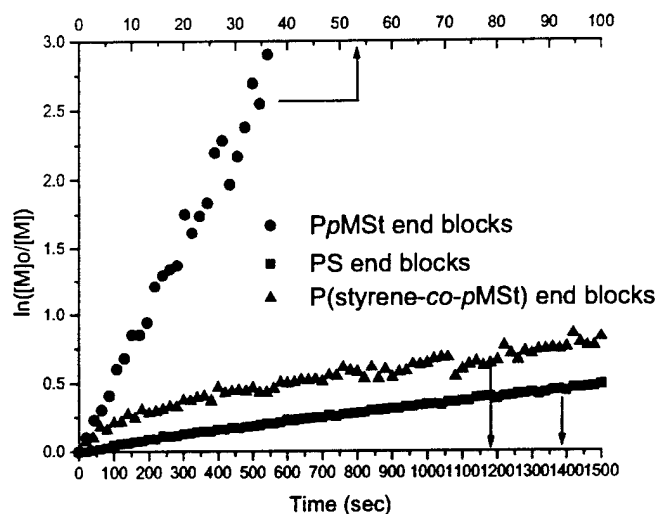
Figure II-6. First order plot of styrene, °MSt and styrene-¼°MSt end block polymerizations

Further studies were conducted using ^{1}H NMR to investigate the microstructure of the end block. Figure II-7 shows the ^{1}H NMR spectrum of the product from the 1:1 styrene:pMSt copolymerization. The peak at 2.35 ppm is due to the methyl groups within °MSt monomer units. The area of this peak, $\beta_{2.5}$, divided by the area of the aromatic resonances between 6 and 8 ppm, $\beta_{i\cdot\pm}$, was used to calculate the fraction of °MSt units in the copolymer, û °MSt, according to Equation II-2.
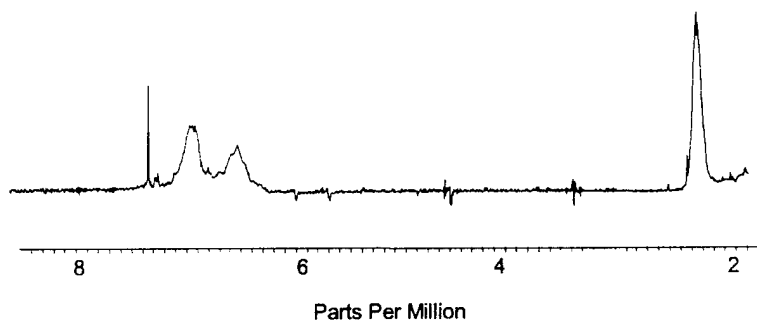

Figure II-7. ^{1}H NMR spectrum of poly(styrene-¼°-methylstyrene)-PIB-of poly(styrene-¼°-methylstyrene).

$$\% \, °\text{ÓÍ} = \frac{5\beta_{2.5}}{3\beta_{i\cdot\pm} + \beta_{2.5}} \times 100\%$$

Eq. II-2

The results shown in Table II-2 indicate that the copolymer end blocks contain a higher percentage of °MSt at low conversions. This causes the unreacted comonomer mixture to become enriched in styrene. This change in concentration allows the styrene to better compete

with the more reactive °MSt monomer and eventually the end block composition approaches a 1:1 ratio at approximately 85 percent conversion.

Table II-2. Composition of Poly(styrene-*co-p*MSt) End Blocks at Various Reaction Conversions

End Block Reaction Time (min)	Conversion	Styrene (%)	*p*-Methylstyrene (%)
0.3	0.07	32	68
1.3	0.14	36	64
135	0.41	39	61
210	0.85	49	51

Preliminary experiments have been conducted in order to synthesize BCPs with untapered poly(styrene-½°MSt) end blocks containing a 1:1 ratio of styrene: °MSt throughout. One technique of interest is monomer starvation in which the styrenic monomer feed is added slowly in a dropwise fashion to the reaction mixture. It is important that the time interval between drops is long enough to allow the more slowly propagating styrene monomer to add to the polymer chain before another drop is introduced to the flask. Upon successful synthesis of such end blocks, the BCPs containing standard and tapered end blocks will be tested and compared in terms of mechanical properties and water transport.

Regardless of the manner in which the styrene and °MSt repeat units are incorporated, it is clear from the GPC traces shown in Figure II-8 that the incidence of coupling was minimized by the incorporation of the °-blocked derivative into the chain. The small peak evident at the high molecular weight side of the main peak has been identified as coupled product. Though the peak is not entirely eliminated, it is significantly diminished as compared to the trace of the BCPs containing homoPS endblocks, indicating fewer coupled chains in the final BCP product.
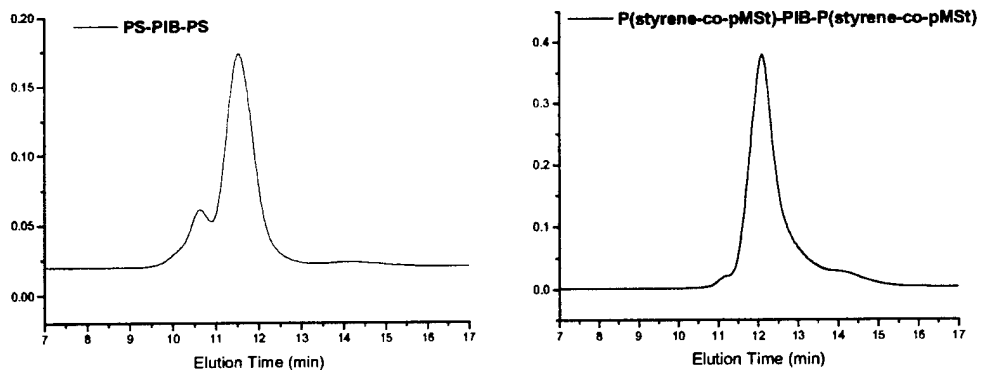

Figure II-8. GPC data from PS-PIB-PS and P(styrene-½°MSt)-PIB- P(styrene-½°MSt) BCPs showing diminished coupling in copolymer end blocks.

E. PRELIMINARY INVESTIGATION OF αMSt-½±°MSt END BLOCKS

Initial studies have also been carried out involving the substitution of styrene with α-MSt. This monomer is also unblocked at the °-position and therefore available for sulfonation. More importantly, the reactivities of α-MSt and °MSt are more comparable to each other (α-MSt is actually slightly more reactive than °MSt) than styrene and °MSt, making the synthesis of an evenly distributed copolymer end block far easier and less time consuming than the monomer starvation technique described above. Of course, the substitution of styrene with αMSt will change polymer properties including the glass transition temperature of the final BCP; however, °MSt will be the predominant comonomer regardless of whether styrene or αMSt is used and will govern the majority of the properties of the end blocks.

Due to overlapping peaks in the ^{1}H NMR spectra of the PIB centerblock and the P(αMSt-½±°MSt) end block, model end block copoylmerizations were conducted using TMP-Cl initiator capped with DPE, in which a monomer charge consisting of a 1:1 ratio of °MSt : α-MSt was added to the reaction flask in one increment. Once again, infrared data of respective end block homopolymerizations were acquired in real time, and aliquots of the copolymerization were collected and analyzed by ^{1}H NMR. Unfortunately, first order plots of the infrared data are noisy due to extremely fast reaction times (See Figure II-9). Although it is clear that α-MSt polymerized slightly faster than °MSt, further experiments are necessary in order to construct plots that will yield reproducible apparent rate constants.

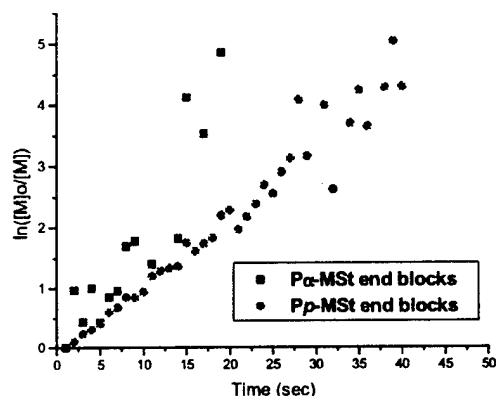Figure II-9. First order plots of α-MSt and °MSt end block homopolymerizations.

Once again, ^{1}H NMR was used to determine the end block composition at various reaction conversions. Figure II-10 shows the ^{1}H NMR spectrum of the product copolymer at full conversion. The peaks at 1.25 and 1.56ppm are due to the methyl groups within αMSt and °MSt repeat units, respectively. The areas under these peaks were integrated and used in Equation II-3 to determine the percent composition of the polymer samples.